



## Full Length Article

# Effect of carbon-interaction on structure-photoactivity of Cu doped amorphous TiO<sub>2</sub> catalysts for visible-light-oriented oxidative desulphurization of dibenzothiophene



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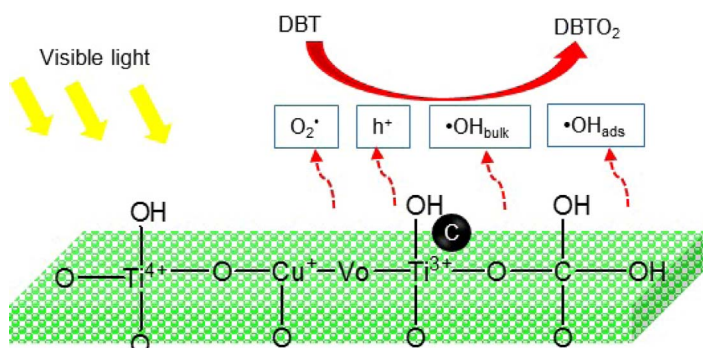
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Amorphous TiO<sub>2</sub> (AT) was successfully prepared via the sol-gel technique, using different titanium sources followed by incorporation of copper via the electrochemical method to give CuO/TiO<sub>2</sub> (CAT) catalysts. The catalysts were characterized via XRD, N<sub>2</sub> physisorption, FTIR, TEM, EDX, XPS, ESR and UV-Vis DRS. The results verified that the use of different titanium precursors have profound effect on the physicochemical properties of the AT catalysts. Further one-pot self-doping carbon from titanium precursor during the addition of copper could greatly enhanced the photocatalytic activity of CAT on the oxidative desulphurization of dibenzothiophene (DBT). 15 CAT<sub>TBOT</sub> exhibited the best performance mainly due to the narrowest band gap and higher numbers of O-Ti-C and Ti-O-C bonds, as well as appropriate amount of Ti<sup>3+</sup> surface defects (TSD). These abovementioned properties offered good mobility of electron-hole pairs and/or trap the electrons for enhancement of photoactivity under irradiation of visible light. Kinetic studies showed that the photocatalytic oxidative desulphurization of DBT followed the pseudo-first order Langmuir-Hinshelwood model, where the adsorption was the

**Abbreviations:** SO<sub>x</sub>, sulphur oxide; TBOT, titanium tetrabutoxide; TTIP, titanium tetraisopropoxide; TEAP, tetraethylammonium perchlorate; V<sub>o</sub>, oxygen vacancies; TSD, Ti<sup>3+</sup> surface defects; PP, potassium peroxodisulphate; TEOA, triethanolamine; SHC, sodium hydrogen carbonate; IP, isopropanol; VB, valence band; CB, conduction band

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controlling step. It is believed that these results could contribute to the synthesis of various supported catalysts for numerous applications specifically in removal of sulphur containing compounds in fuel oils.

## 1. Introduction

The release of  $\text{SO}_x$  which mainly formed via the burning of sulphur-containing compounds in fuel oils is one of the most serious worldwide environmental concerns [1]. In order to minimize its harmful influence on human health and the environment, the reduction of sulphur content in fuel is urgently required [2–4]. Photocatalytic degradation process using heterogeneous catalysts is fascinating and prominent for environmental protection as an environmental friendly, low cost, and sustainable technology [5]. Among photocatalytic materials,  $\text{TiO}_2$  is widely used for degradation of dyes and organic pollutants, as well as for the removal of inorganic materials due to its excellent photoactivity [6]. However,  $\text{TiO}_2$  only responds to ultraviolet radiation due to its large band gap (3.2 eV) and fast electron-hole recombination rate, which causes difficulties with respect to its practical application [7]. As a result, great effort has been expended toward the improvement of new visible-light-responsive photocatalysts.

Among the various types of  $\text{TiO}_2$  catalysts, amorphous  $\text{TiO}_2$  nanoparticles have experienced intensive advances, and a growing number of studies have started to challenge the belief that the amorphous  $\text{TiO}_2$  is not photoactive [8]. As compared to crystalline  $\text{TiO}_2$ , amorphous  $\text{TiO}_2$  is easily prepared, owing to its lower demand of substrate [9]. It also does not require heat treatment processes, and may allow the use of a much wider range of dopants. Amorphous  $\text{TiO}_2$  has been used for various photocatalytic reactions such as hydrogen evolution from water, decolourization of methylene blue and disinfection of algae blooms, as well as oxidative desulphurization of dibenzothiophene [10–12].

Previous study showed that the use of different titanium precursor to synthesize amorphous  $\text{TiO}_2$  has contributed to dissimilar pore size distribution and surface area [13]. The presence of long chain carbon might reduce hydrolysis and condensation rate and restrict the particle nucleation, thus yields aggregated bigger particles with small surface area and high pore volume. During hydrolysis, Ti-alkoxide react with water to form  $\text{Ti}(\text{OH})_4$  and alcohol, which subsequently polymerized to a three-dimensional oxide network [14]. The alcohol group that formed after hydrolysis process are determined by the carbon chain of alkoxide and subsequent drying or calcination might remove these species.

Recently, it has been reported that band gap modification via non-metal doping such as C, N, S, F and B can produce highly active  $\text{TiO}_2$  photocatalysts [15]. Non-metal doping is a promising way to enhance the photoabsorption properties of  $\text{TiO}_2$  by lowering the band gap and shift the absorption edge to the visible light region [16]. It is believed that bulk doping or matrix substitution can introduce interior electron states within the band gap and thus shift the response and harvest visible light for applications in photocatalysis [17]. In addition, the combination of  $\text{TiO}_2$  with other semiconductors with narrow band gaps is also an efficient pathway to extend the visible light response of  $\text{TiO}_2$ -based catalysts. For coupling with  $\text{TiO}_2$ , nanosized CuO is an ideal candidate due to its proper band edge, low cost, low toxicity, and abundant supply [18].

In recent years, numerous nanosized particles of ZnO,  $\alpha$ -FeOOH and NiO supported on mesostructured silica nanoparticles (MSN), Ag supported on mesoporous  $\text{TiO}_2$  nanoparticles (MTN) and also CuO supported onto carbon nanotubes (CNT) were successfully prepared via a facile electrochemical technique [19–22]. Their excellent performances in the photocatalytic degradation of dyes and organic pollutants, along with  $\text{CO}_2$  reforming of  $\text{CH}_4$ , would encourage additional modification. In previous work, the electrochemical method provided a stronger interaction between the dopant and support, and consequently lessened

the agglomeration of dopant, thus forming uniform and smaller dopant particles [23]. Therefore, herein we report new findings on (i) self-doped C via the electrochemical method for synthesis of CuO loaded onto AT catalysts, and (ii) their enhanced performance towards photocatalytic oxidative desulphurization of DBT under visible light irradiation. The physicochemical properties of the catalysts were well characterized by X-ray diffraction (XRD),  $\text{N}_2$  physisorption, Transmission electron microscopy (TEM), energy dispersive X-ray (EDX), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS). The proposed structure of the catalyst, kinetic studies, and the proposed mechanism of photo-oxidative desulphurization are also discussed. We believe that this study could contribute to future design approaches for numerous organic pollutants and other reactions.

## 2. Experimental

### 2.1. Materials

Titanium tetrabutoxide (TBOT) was purchased from Merck Sdn. Bhd., Malaysia. Other chemicals used were similar with those used and prepared by earlier reported studies [24,25].

### 2.2. Synthesis of catalyst

The amorphous  $\text{TiO}_2$  was synthesized by sol-gel technique using TTIP or TBOT as titanium precursor and denoted as  $\text{AT}_{\text{TTIP}}$  and  $\text{AT}_{\text{TBOT}}$ , respectively [25]. The CuO/ $\text{TiO}_2$  amorphous were synthesized via electrolysis method using  $\text{AT}_{\text{TBOT}}$  as support, based on previous reported study with some modification [25–27].

### 2.3. Characterization of the catalyst

The structural properties of the catalysts were determined with X-ray diffraction (XRD) recorded on powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a  $\text{Cu K}\alpha$  radiation source. Beckman Coulter SA 3100 surface area analyzer was used in  $\text{N}_2$  physisorption analysis to study the textural properties which is conducted at 77 K. Prior to measurement, the samples were degassed at 373 K for 1 h. The Brunauer-Emmett-Teller (BET) method was used to calculate surface area from the  $\text{N}_2$  adsorption isotherms. FTIR was performed by the KBr method using PerkinElmer Spectrum GX FTIR spectrometer in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Transmission electron microscopy (TEM) was used to examine the morphological properties using JEOL JEM-2100F while energy dispersive X-ray (EDX) was carried out to identify the chemical composition of the catalysts. The X-ray photoelectron spectroscopy (XPS) was conducted on a Shimadzu Axis Ultra DLD spectrometer, using Al X-ray source over binding energies of 0–800 eV to determine the chemical oxidation of the catalyst. The electron spinning resonance (ESR) analysis was performed using JEOL JESFA100 ESR spectrometer at room temperature. UV–Vis diffuse reflectance spectra (UV–Vis DRS) using a PIKE Technologies DiffusIR in the range of 300 to 800 nm was conducted at room temperature to examine the band gap of the catalysts.

### 2.4. Photocatalytic oxidative desulphurization reaction

The photocatalytic oxidative desulphurization of dibenzothiophene (DBT) were carried out in a batch reactor as reported in our previous

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